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Hydrogenation of bisphenol A – Using a mesoporous silica based nano ruthenium catalyst Ru/MCM-41 and water as the solvent

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ABSTRACT

A green approach to the hydrogenation of bisphenol A (BPA) including the selection of catalysts and solvents was demonstrated in this report. The catalyst preparation was also using a simple and green method for synthesizing a silica-supported ruthenium catalyst (Ru/MCM-41) in supercritical carbon dioxide. The characterizations of the Ru/MCM-41 nanocomposites were preformed by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The nanoparticles have an average size of 3.4 nm which is smaller than the pore size of MCM-41. The hydrogenation of BPA was carried out in a hydrogen pressure of 50 bars and a temperature range from 75 to 85 °C with different catalysts and solvents combinations. It was found that using the synthesized catalyst Ru/MCM-41 in water medium could achieve the highest efficiency and durability for the hydrogenation of BPA.

1. Introduction

Bisphenol A (BPA; 4,4′-isopropylidenediphenol) is an universal starting material for making plastic products. A representative application is to use BPA to synthesize epoxy resins. The BPA type epoxy resins could be used for light-emitting diode (LED) encapsulation due to their chemical resistance, mechanical and electrical strength associated with excellent thermal stability. However, the aromatic groups in the epoxy resins are susceptible to yellowing upon ultraviolet (UV) light exposure or thermal degradation causing an interference of the LED transmission through the epoxy resins [1]. On the other hand, BPA made polycarbonate plastic is also widely used in daily products such as food containers. The health concerns of BPA have drawn much attention in recent years since BPA is labeled as an endocrine disruptor [2]. Therefore, a practical solution is to apply hydrogenated bisphenol A (HBPA; 4,4′-isopropylidenedicyclohexanol), which does not contain the aromatic groups, to substitute the general usage of BPA. HBPA is not an endocrine disruptor and does not cause yellowing when used in epoxy resin for the LED chip packaging since there are no aromatic groups available to absorb the UV light. There are several reports studying the hydrogenation reaction of BPA. A pioneering study by Terada proposed the mechanism of the hydrogenation of BPA which was catalyzed by nickel catalysts [3]. Maegawa et al. [4] used commercial rhodium and ruthenium on activated carbon catalysts to hydrogenate BPA in isopropanol solvent. Their results showed that under mild hydrogen pressure and temperature conditions, the Rh/C catalyst was more efficient than the Ru/C catalyst. Wang et al. [5] studied the hydrogenation of BPA using Al_2O_3-supported noble metal catalysts. In their continuous reaction system, the product selectivity towards HBPA was more than 94%. To the best of our knowledge, the hydrogenation of BPA using water as a solvent has not been reported before. The advantage of using water as a green solvent is well known [6–9]. In brief, water is nontoxic, nonflammable and easy to obtain. To achieve an ideal green reaction by using water as the solvent, insoluble products are more preferable since they could be easily separated by precipitation or filtration. Thus the water solvent may maintain its purity and cleanness for further using without producing any additional aqueous waste. Moreover, if possible, it would be an advantage to have accelerated reaction rates when using water as the solvent comparing to using other organic solvents. In this study, the reactant BPA and the product HBPA are both sparingly soluble in water (<300 ppm at 21.5 °C). It was observed that they form a suspension (estimated solubility 1000 ppm) in hot water with stirring [10]. Therefore, the BPA hydrogenation in water may be considered as an ideal green reaction. Herein this manuscript, some examples of hydrogenation of aromatic compounds in water were reported by using gaseous hydrogen as the hydrogen source. This is somewhat different from the transfer hydrogenation reactions that have been reported in

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the literature [11,12]. In addition, the catalyst used in this study is a mesoporous silica based nano ruthenium catalyst Ru/MCM-41. It was prepared by a simple supercritical fluid deposition method which has also been considered as a green process [13]. The selection of a silica based catalyst also proves to be adequate for the hydrogenation reaction in water.

2. Experimental

2.1. Catalyst preparation

Cyclic ligand metal precursors were used as the CO_2-soluble metal precursors in this study. Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium [Ru(cod)(thmd)$_2$, Strem], MCM-41 (SiO_2, Sigma–Aldrich) were all used as received. In a typical trial, 285 mg of MCM-41 and ca. 87 mg of Ru(cod)(thmd)$_2$ were added together into a high pressure cell for a maximum metal ratio of 5% by weight. At 150 °C, 100 bar of H_2 and 100 bar of CO_2 were premixed in a gas reservoir and injected into the cell for a reaction of 2 h. After the reaction, the cell was depressurized and flushed with CO_2 for a few times to eliminate the unreacted metal precursors. The remaining powder sample was then collected for further analysis and catalytic testing.

2.2. Catalyst characterization

2.2.1. Transmission electron microscopy

The images of transmission electron microscopy (TEM) were taken by Joel JEM-2100. The synthesized catalyst powder was diluted with ethanol and ultrasonicated for 5 min. Droplets of the prepared solution were put on a copper grid and dried in a vacuum oven of 100 °C overnight. The statistics calculations of the particle size distribution were made by using an interactive imaging software OPTIMAS5. At least 100 particles were recorded in order to obtain the average particle size and standard deviation.

2.2.2. Powder X-ray diffraction

Powder X-ray diffraction (XRD) was conducted by Rigaku Ultima IV. The Cu Kα radiation was 40 kV, 20 mA. The scan rate was 1°/min starting at 10° to 90° (2θ).

2.2.3. Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDS) was measured by Oxford 6587 which was coupled with a scanning electron microscope (SEM JEOL JSM-5600). The quantitative analysis of the ruthenium content in the nanocomposite was taken at least 5 different sample points into average.

2.2.4. BET measurements

The BET measurements were based on N_2 adsorption by Micromeritics ASAP 2010. The outgas condition was 200 °C, 24 h.

2.3. Hydrogenation of BPA and other aromatic compounds

The experimental apparatus for the aqueous hydrogenation of BPA is a semi-batch system. Ruthenium on activated carbon [5% Ru/C, Strem], isopropanol [HPLC-grade 99.9% IPA, Echo] and 4,4′-isopropylidenediphenol [BPA 99+%, Sigma–Aldrich] were all used as received. In a typical trial, a mixture of 50 mg of the catalyst, 1 g of the BPA and 50 g of deionized water were all added into a high pressure autoclave. Hydrogen gas of 50 bar was then introduced into the cell at temperature of 75 °C for a reaction time of 5 h. The data points were collected after the reaction system was depressurized and cooled down to room temperature. The products were then determined by gas chromatography–mass spectrometry (GC–MS; HP5890II/HP5972). A dimethylpolysiloxane based GC capillary column (Agilent HP-5MS) was used. The injector and the detector temperatures were set at 250 °C and 260 °C, respectively. A temperature program was employed for analysis starting at 50 °C (hold for 5 min), followed by a 10 °C/min program rate to 250 °C (hold for 5 min). The product, 4,4′-isopropylidenedicyclohexanol [HBPA 97%, Sigma–Aldrich] was used as an analytical standard.

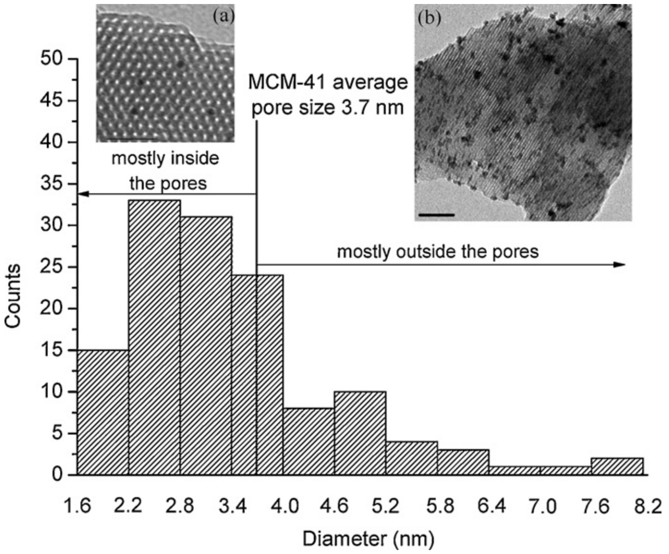

Fig. 1. TEM images and statistics calculation of the synthesized Ru/MCM-41 nanocomposite. (a) Particles mostly inside the pores, scale bar = 20 nm; (b) particles mostly outside the pores, scale bar = 50 nm.

3. Results and discussion

3.1. Catalyst preparation and analysis

The preparation method of the catalyst using supercritical carbon dioxide was previously reported with some minor changes [14,15]. The metal precursor used in our previous study was a beta-diketonate ruthenium compound, ruthenium acetylacetonate [Ru(acac)$_3$]. The metal beta-diketonate compounds usually have lower solubility in CO_2 than those of metal cyclic compounds [16]. Therefore, in our previous work, the addition of an organic solvent was necessary to help dissolve and disperse the metal precursor. In this current study, the organic solvent can now be excluded due to the higher solubility of the cyclic metal precursor. As expected, the synthesized ruthenium nanoparticles on MCM-41 by the two different precursors were nearly identical in chemical catalytic activity since they were similar in both metal loading and particle size [17]. In order to achieve a greener approach, the metal cyclic compound, Ru(cod)(tmhd)$_2$ was chosen as the precursor for the current research [18].

The support, MCM-41, was invented by Mobil company in 1992 and it has a 2 dimensional tubular structure with meso-size pores on both ends [19]. The TEM images of the catalyst Ru/MCM-41 and the statistics calculations of the particle size are shown in Fig. 1. More than 100 particles were measured in order to obtain the average size 3.4 nm. It could be observed that the smaller ruthenium nanoparticles were grown inside the pores of MCM-41 (Fig. 1a) while the bigger clusters were only attached to the outer part of the support (Fig. 1b). The physical properties of the support MCM-41 were provided by both the manufacturer and our experimental values which are listed in Table 1.

From EDS analysis, the Ru metal loading was found to be 3.7% by weight. The oxygen to silicon atomic ratio, however, was increased from the expected value 2 (silica is SiO_2) to nearly 3. This could

Table 1
Physical properties of MCM-41.

MCM-41	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Sigma–Aldrich	1000	2.3–2.7	0.98
Experimental	1214	3.7	1.14

imply that the adsorption of water molecules occurred on the silica surface since silica is a well known water adsorbent. According to the literature, the water molecules could be removed by the supercritical fluid treatment and free hydroxyl groups could be created on the silica surface [20]. These hydroxyl groups may help adsorb the metal precursors on the silica. The overall yield of the supercritical fluid deposition process could also be calculated and an efficient 75% yield (from maximum metal loading 5%) was obtained. Reproducibility of the catalyst was also examined and the overall yield was within a ±5% range.

The powder XRD analysis of the Ru/MCM-41 is shown in Fig. 2. The broad peak between 15° and 30° can be assigned to the silica support, MCM-41. Ruthenium has a hexagonal closed-packed (hcp) structure and the major peak (1 0 1) is located at 44.0° (2θ). All of the analyses mentioned above could confirm that the Ru nanoparticles were deposited on the mesoporous silica support, MCM-41.

3.2. Solvent selection for the hydrogenation of BPA using Ru/MCM-41

The hydrogenation of BPA using the synthesized catalyst Ru/MCM-41 was conducted in different types of common solvents including water, a non-polar solvent: cyclohexane, a polar aprotic solvent: ethyl acetate and a polar protic solvent: isopropanol. The experimental results are listed in Table 2. The turnover frequency (TOF) was calculated as the moles of hydrogen consumed in 1 h (1 mole of H_2 for 1 mole of C=C double bond) divided by the total moles of metal inside the catalyst. It is unexpected to see that the reaction proceeded most rapidly in water. Normally, the dielectric constant of a solvent is one of the first considerations for the solvent selection. In the case for hydrogenation, solvents with lower dielectric constant would be preferred since the solubility of hydrogen in these solvents would be higher. On the other hand, the reactant BPA is almost insoluble in water and cyclohexane, whereas it is completely soluble in ethyl acetate and isopropanol. Regardless of all the disadvantages mentioned above, water provides a suitable environment for the silica based catalyst to disperse thoroughly in the reaction medium. It is suggested that the hydroxyl groups on the silica surface could form hydrogen bonding with the water molecules [21]. The hydrogen bonds could help the water molecules surround the catalyst surface thus creating a better dispersion of the catalyst. Therefore, water was demonstrated to be a suitable solvent for the hydrogenation of BPA using Ru/MCM-41.

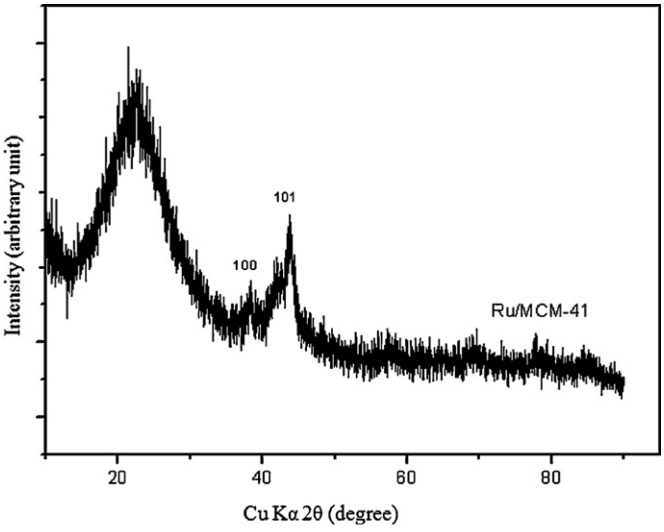

Fig. 2. XRD pattern of the synthesized Ru/MCM-41.

Table 2
Comparison of different solvents used for the hydrogenation of BPA[a].

Solvent	Dielectric constant	Conversion (%)	HBPA yield (%)	TOF[b] (h^{-1})
Cyclohexane	2.02	21.3	7.9	41
Ethyl acetate	6.02	12.7	0.6	19
Isopropanol	18	44.4	8.7	74
Water	80	97.0	51.0	207
Water	80	99.6	91.9	342[c]

[a] Ru/MCM-41: 50 mg; solvent: 50 g; BPA: 1 g; H_2: 50 bar; temperature: 75 °C; reaction time: 5 h.

[b] Turnover frequency (TOF) was calculated as the moles of hydrogen consumed in 1 h (1 mole of H_2 for 1 mole of C=C double bond) divided by the total moles of metal inside the catalyst.

[c] 85 °C, 4 h.

3.3. Effect of solubility in water for the hydrogenation of BPA

Since the major portion (about 95%) of the reactant does not dissolve in water, it is believed that the concentration of the reactant should be saturated when adjusting the water amount in the system. From Table 3, the water amount was doubled to the previous experiment with all other conditions maintained. As a result, the conversion was still maintained close to completion while the HBPA yield and TOF both decreased with the addition of water. A possible explanation is that the concentrations of the reactant and the catalyst were diluted by the additional amount of water and the effective collisions between them during the reaction were reduced. This outcome showed that the solubility of the reactant was not the limitation for the reaction since the amount of the fully converted reactant was far more than the amount of the dissolved reactant. The low solubility of the product should not have a negative influence to the reaction either since it could be separated out of the system easily. Another possibility is the occurrence of the “on-water” reaction [8]. The insoluble reactants could directly participate in the reaction which could increase the reaction rate. Therefore, it is unnecessary to use more amount of water for our selected conditions. For green chemistry, it is also very important to reduce the water amount for the hydrogenation process since water is a valuable natural resource.

3.4. Catalyst selection and recyclability for the hydrogenation of BPA in water

The next series of experiments were designed to confirm if Ru/MCM-41 is a suitable catalyst for the hydrogenation of BPA in water. For comparison, a commonly used 5% Ru/C commercial catalyst was chosen for the testing. According to the literature, carbon or charcoal supports usually have better catalytic activity than oxide supports in hydrogenation reactions under various solvents [22]. From our experimental results, which are shown in Fig. 3, it was dif-

Table 3
Comparison of different water amount for the hydrogenation of BPA[a].

Water amount (g)	Conversion (%)	HBPA yield (%)	TOF (h^{-1})
50	99.6	91.9	342
100	97.9	67.8	290

[a] Ru/MCM-41: 50 mg; BPA: 1 g; H_2: 50 bar; temperature: 85 °C; reaction time: 4 h.

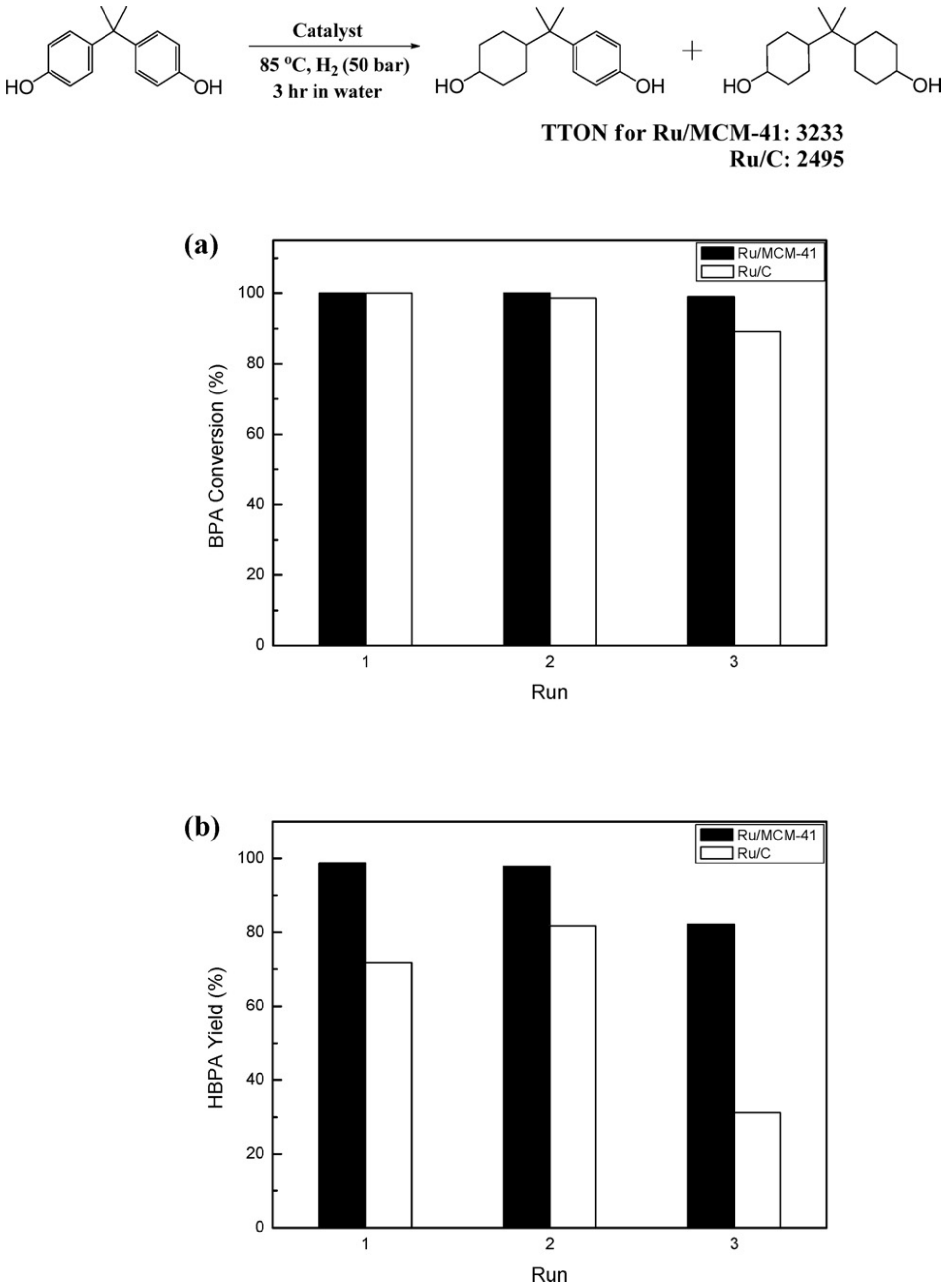

Fig. 3. Reusing of the catalysts for the hydrogenation of BPA. (a) The conversion percentage of BPA; (b) the yield of HBPA. TTON is defined as the total moles of hydrogen consumed in the three runs combined (1 mole of H_2 for 1 mole of C═C double bond) divided by the total moles of metal inside the catalyst. Note that the metal content of Ru/MCM-41 was increased to 4.7% in order to be more comparable with the commercial 5% Ru/C catalyst.

ficult to distinguish the catalytic activity of the two catalysts during the first runs since the conversion of the reactions were both close to completion (Fig. 3a Run 1). Therefore, we changed the strategy to examine the recyclability of the catalysts which is related to the catalytic activity over time. Additional runs of tests were added in order to study the recyclability of the catalysts. It is important to reuse the catalysts, especially heterogeneous ones, not only for the environmental purpose but also for the economical purpose. Two different recycling methods suitable for silica based catalysts were reportedly available. The first method was using a rotary evaporator to discard the water solvent after the reaction. Ethanol was added thereafter to the slurry type residue to dissolve the products so that the catalyst could be removed by filtration [23]. The other method was a direct extraction by diethyl ether of the product out of the water layer [4]. Since BPA and HBPA are both nearly insoluble in water, using small amount of organic solvent which is immiscible in water could extract the compounds completely without removing the catalysts out of the water phase. Thus the water phase including the catalyst could be used repeatedly [24]. However, it is a pity that the direct extraction method could not be applied when using carbon supported catalysts. Since the hydrophobicity of the carbon surface have higher affinity to the organic phase, the carbon catalyst would be extracted out of the water phase along with the products. Therefore, only the first recycling method using rotary evaporator was selected in this study. From Fig. 3a, the conversion of the reaction in the first three runs could be kept to completion when using both catalysts, although there was a slight decrease during the third run when using Ru/C. If focusing on the yield of the product HBPA, shown in Fig. 3b, the difference of the two catalysts would be clearer. In the case of Ru/C, the HBPA yield had a huge drop in the

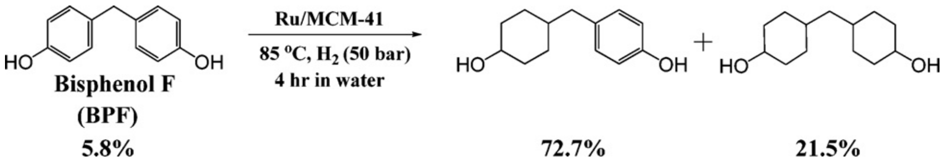

Fig. 4. The hydrogenation of BPF (BPF: 1 g; Ru/MCM-41: 50 mg; water: 50 g; TOF = 337 h^{-1}).

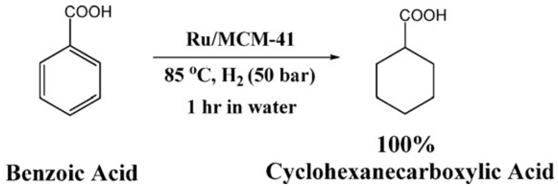

Fig. 5. The hydrogenation of benzoic acid (benzoic acid: 1 g; Ru/MCM-41: 50 mg; water: 50 g; TOF = 1329 h^{-1}).

third run which was corresponding to the decrease in conversion. For Ru/MCM-41, the HBPA yield were close to maximum in the first two runs and started to have a small decrease in the third run. Nevertheless, the HBPA yields were always higher by using Ru/MCM-41 than those by Ru/C. The other product, 2-(4-hydroxycyclohexyl)-2-(p-hydroxyphenyl)propane, was considered as the intermediate of the reaction since only one benzene ring of BPA was hydrogenated. No other compounds were detected so that the conversion of BPA was equal to the total yield of the two products. Comparing the total turnover number (TTON) is an apparent way to evaluate the durability of the catalysts. It is a useful information to know how many reactants the catalyst can convert before losing its catalytic activity. Here, the TTON is defined as the total moles of hydrogen consumed in the three entries combined (1 mole of H_2 for 1 mole of C=C double bond) divided by the total moles of metal inside the catalyst. With a lower TTON value, it is no surprise to see the catalytic activity of Ru/C being inferior to that of Ru/MCM-41. As mentioned before, the hydrophilic property of the silica support causes the entire catalyst to have a better dispersion in the water phase than the hydrophobic type carbon supported catalyst. According to some reports, the hydroxyl groups from the surface of silica may have a strong interaction, such as hydrogen bonding, with the reactants [25,26]. More contacts between the reactant and the catalyst would occur with the assistance of the strong interaction thus increasing the reaction rate. Moreover, the declining activity for both catalysts should be attributed to the leaching and poisoning of the ruthenium metal in water. To summarize this section, the silica supported catalyst was proven to be a more durable catalyst for the hydrogenation reaction in water.

3.5. *Hydrogenation of other aromatic compounds in water*

Another compound from the bisphenol chemical family, bisphenol F (BPF; 4,4′-methylenediphenol), was tested for the hydrogenation reaction and the results are shown in Fig. 4. The properties of BPF are quite similar to BPA in terms of molecular weight, melting point and solubility in water. A popular application of BPF is to blend it with BPA to make a mixed typed epoxy resin which has a lower viscosity than the pure BPA type epoxy resin. The calculated TOF values of BPA and BPF were nearly identical which was expected and could represent that the two methyl groups on the center carbon do not have much of steric hindrance on the reaction.

To our interest, a single aromatic ring compound, benzoic acid, was also chosen for the testing (Fig. 5). The calculated TOF value of benzoic acid was much improved and could be mainly due to the molecular size and structure of the compound. The smaller size of the benzoic acid molecules not only can penetrate faster into the pores of MCM-41 but also can have less occupation of the active surface of the metal nanoparticles. Furthermore, since there is only one aromatic ring in benzoic acid, all the C=C double bonds are coplanar which are readily for the syn addition of the hydrogen atoms. In BPA and BPF, however, the two aromatic rings would have more difficulties for this type of concerted reaction. Consequently, the synthesized Ru/MCM-41 catalyst is very efficient for the hydrogenation of various reactants in water solvent.

4. Conclusion

The hydrogenation of water insoluble compounds such as BPA and BPF has been successfully demonstrated using water as the solvent. From the measured experimental data, the low solubility of the reactants in water was found not to be the limitation for the reactions. On the other hand, the low solubility of the products in water could simplify the work-up process of the reaction by filtration or precipitation. In addition, the nanocomposite Ru/MCM-41 has been synthesized and applied as a catalyst for various hydrogenation reactions in water. The catalytic activity and the durability of the Ru/MCM-41 catalyst were tested to be superior to a commercial carbon supported catalyst due to better dispersion and recyclability of silica in water. Last but not least, the combination of applying a supercritical fluid technique for the catalyst preparation and a reaction in water medium could make the overall process "greener" which is the ultimate goal of green chemistry for a future sustainable world.

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